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OPTICAL PROPERTIES OF A MECHANICALLY POLISHED AND AIR-EQUILIBRATED [111] UO2 SURFACE BY RAMAN AND ELLIPSOMETRIC SPECTROSCOPY

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Optical properties of a mechanically polished and air-equilibrated [111] UO_2 surface by Raman and ellipsometric spectroscopy.

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Abstract. Optical constants of a [111] UO_2 surface, aged in air, were measured in the range from .8 and 5 eV using ellipsometric spectroscopy. The ellipsometric data acquired at angles of incidence of 65, 70 and 75 degrees have been fitted by two techniques: 1) First at low energies with a Cauchy-Urbach model extended by the point by point method to higher energies and shown to be Kramers-Kronig consistent, 2) by a Gauss-Lorentz and a Tauc Lorentz Oscillator. Both techniques lead to dielectric constants that differ at energies above 2 eV substantially from Schoenes' for vacuum-annealed [111] UO_2. Raman spectra taken at 632 nm show no indication of hyper-stoichiometry.

1. Introduction

Properties of uranium oxide are of interest in all areas of the nuclear industry. The optical properties of vacuum-annealed signal crystal UO_2 have been determined from near-normal reflectance spectroscopy data by Schoenes [1], [2] [3] and compared to the electronic structure of UO_2. UO_2 encountered in practical situations has been exposed to air. Here we analyze a UO_2 single crystal that has been exposed to air for 25.5 years. R. Schulze of Los Alamos National Laboratory has provided the crystal.

2. Experimental Procedure

The sample was mechanically polished in 1983 and has been exposed since then to laboratory air. It was analyzed in air using a WVASE ellipsometric Spectrometer equipped with a 75-watt light source and a HS-190 monochrometer [4]. Ellipsometric data Δ and Ψ were collected at 65°, 70°, and 75° angle of incidence at photon energies between .75 and 5.5 eV. Several runs were performed with and without source-beam collimator (producing different sizes of incident beams) and different iris openings of the detector. The results were indistinguishable. The data were modeled by two techniques: 1) by a Cauchy model with Urbach extension in the low energy range below 2 eV, extended to higher energies by the point by point method and checked thereafter for Kramers-Kronig consistency. In the Cauchy model the index of refraction n and the extinction coefficient k are given by

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^3} + .., \; k(\lambda) = Amp_k e^{Exponent_k * (E - E_k)}, \; E = \frac{1240}{\lambda}, \qquad (1)$$

2) by fitting two oscillators, a Gauss-Lorentz for the low-energy and a Tauc-Lorentz Oscillator for the high-energy range directly to the data. A Gaussian oscillator has the form

$$\varepsilon_2(E) = Amp\left(e^{-\left(\frac{E-E_n}{\sigma}\right)^2} - e^{-\left(\frac{E+E_n}{\sigma}\right)^2}\right), \quad \sigma = \frac{\mathrm{Br}}{2\sqrt{\ln(2)}} \tag{2}$$

Fit parameters are the amplitude *(Amp)*, the center energy *(E_n)* and the broadening *(Br)* of the absorption peak. *Br* equals the Full-Width-Half-Maximum (FWHM) value. Gauss-Lorentz and Tauc-Lorentz oscillators have additional parameters. The quality of the fit is describe by

$$MSE = \sqrt{\frac{1}{2N-M}\sum_{n=1}^{N}\left[\left(\frac{\Psi_i^{\mathrm{mod}} - \Psi_i^{\exp}}{\sigma_{\Psi,i}^{\exp}}\right)^2 + \left(\frac{\Delta_i^{\mathrm{mod}} - \Delta_i^{\exp}}{\sigma_{\Delta,i}^{\exp}}\right)^2\right]}, \mathrm{M} = \text{Number of parameters} \tag{3}$$

Raman spectroscopy using 632nm light was performed at low and high resolution to check the oxidation state of the sample.

3. Experimental Results

The Raman spectrum (see figure 2) showed no indication of hyperstochiometry. The Cauchy-Urbach fit produced the parameters An=2.2715, Bn=.1993, Cn=.055061, Amp_k=1.7835, $Exponent_k$=1.3794 and an excellent MSE value of 1.092. (See equations 1 and 3). The Tauc-Lorentz oscillator had the parameters: Amp1=130.8, C1=2.1538, E1offset=1.8572, En1=3.5646, Eg1=2.7289, and the Gauss-Lorentz oscillator had the parameters: Amp2=2.2015, En2=2/4467. PoleMag.0=.45405, Br2=1.7716, PolePos.0=5.8396, PoleMag2=.010032, Pole Pos2=.70399. The MSE value of the oscillator fit was 5.238, a value considered to be indicative of a good fit. The different types of fit produced indistinguishable results. Figure 3 shows our dielectric constants e1 and e2 together with those of Schoenes, and figure 4 the optical constants n and k as a function of energy or wavelength. Table 1 lists the dielectric constants e1 and e2 as a function of energy.

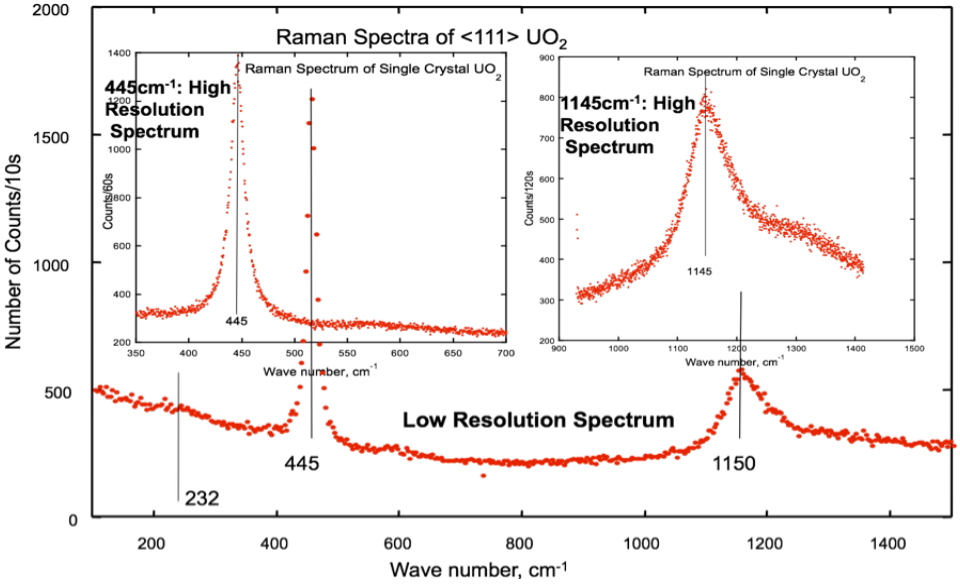

Figure 2. The Raman spectrum taken at high and low resolution using 632 nm laser light.

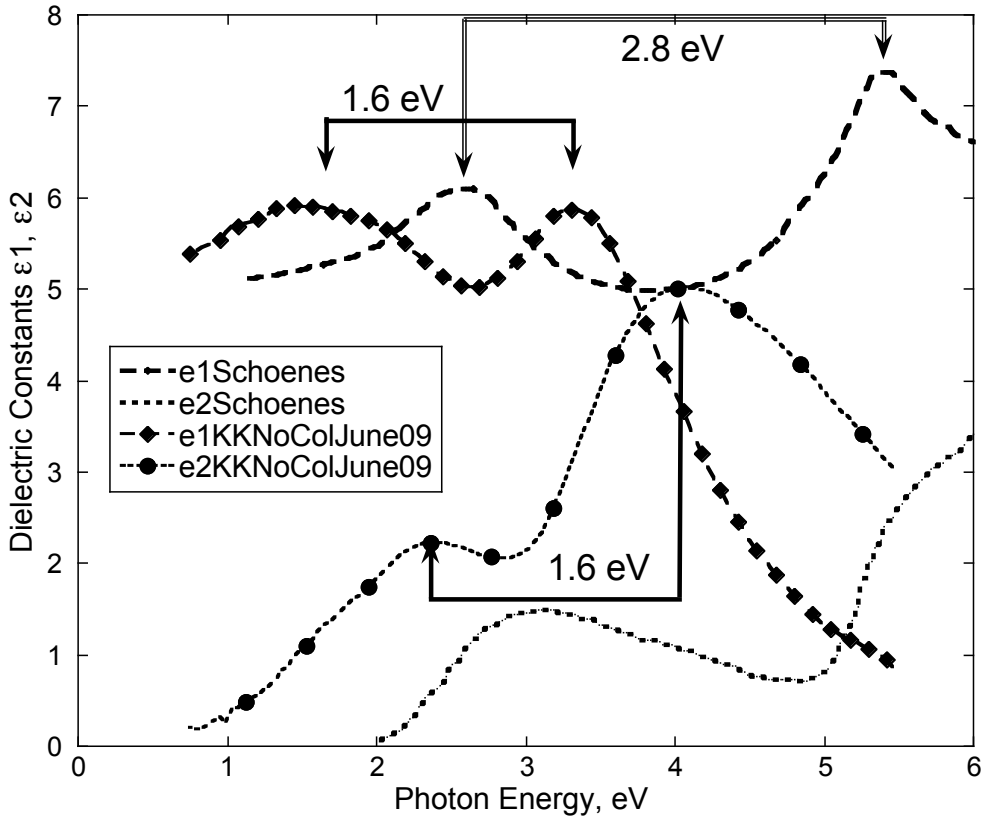

Figure 3. Comparison of our results derived from spectroscopic ellipsometry with Schoenes' results derived from near-normal reflectance data.

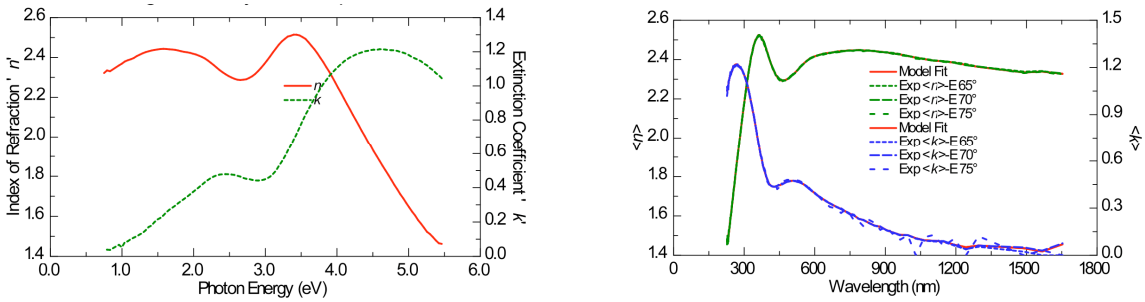

Figure 4. The optical constants n and k as a function of energy or wavelength.

Table 1. The dielectric constants ε1 and ε1 of [111] UO_2 exposed to air for 25.5 years

eV	ε1	ε2	eV	ε1	ε2	eV	ε1	ε2
5.462	0.8978	3.089	3.891	4.341	4.936	2.362	5.274	2.201
5.421	0.9759	3.130	3.850	4.509	4.878	2.321	5.334	2.194
5.379	1.040	3.175	3.809	4.665	4.802	2.279	5.401	2.172
5.338	1.035	3.211	3.767	4.819	4.730	2.238	5.465	2.141
5.297	1.042	3.338	3.726	4.979	4.641	2.197	5.531	2.101
5.255	1.076	3.406	3.685	5.121	4.522	2.155	5.590	2.041
5.214	1.113	3.496	3.643	5.271	4.444	2.114	5.638	1.979
5.173	1.144	3.579	3.602	5.425	4.292	2.073	5.679	1.919
5.131	1.202	3.684	3.561	5.552	4.147	2.031	5.713	1.851

5.090	1.259	3.709	3.519	5.674	3.982	1.990	5.743	1.789
5.049	1.280	3.794	3.478	5.765	3.794	1.949	5.768	1.727
5.007	1.317	3.869	3.437	5.835	3.621	1.907	5.790	1.665
4.966	1.363	3.961	3.395	5.893	3.432	1.866	5.808	1.604
4.925	1.421	4.036	3.354	5.907	3.223	1.825	5.828	1.547
4.883	1.498	4.147	3.313	5.915	3.088	1.783	5.844	1.490
4.842	1.577	4.179	3.271	5.913	2.883	1.742	5.869	1.441
4.801	1.631	4.255	3.230	5.872	2.731	1.701	5.896	1.368
4.759	1.711	4.334	3.189	5.833	2.594	1.659	5.909	1.296
4.718	1.793	4.403	3.147	5.781	2.447	1.618	5.932	1.244
4.677	1.881	4.472	3.106	5.708	2.322	1.577	5.937	1.136
4.635	1.980	4.536	3.065	5.619	2.208	1.535	5.934	1.093
4.594	2.082	4.580	3.023	5.519	2.137	1.494	5.946	1.007
4.553	2.173	4.630	2.982	5.428	2.088	1.453	5.928	0.9237
4.511	2.262	4.676	2.941	5.347	2.058	1.411	5.927	0.8839
4.470	2.366	4.743	2.899	5.277	2.036	1.370	5.928	0.7797
4.429	2.480	4.789	2.858	5.213	2.033	1.329	5.896	0.7028
4.387	2.587	4.829	2.817	5.160	2.035	1.287	5.847	0.6281
4.346	2.706	4.885	2.775	5.125	2.053	1.246	5.826	0.6198
4.305	2.834	4.911	2.734	5.097	2.051	1.205	5.817	0.5227
4.263	2.959	4.957	2.693	5.070	2.078	1.163	5.760	0.4603
4.222	3.100	4.987	2.651	5.059	2.096	1.122	5.714	0.4408
4.181	3.239	4.998	2.610	5.060	2.127	1.081	5.711	0.4201
4.139	3.383	5.018	2.569	5.075	2.151	1.039	5.695	0.3206
4.098	3.528	5.023	2.527	5.098	2.170	0.9980	5.602	0.2437
4.057	3.678	5.030	2.486	5.129	2.188	0.9567	5.540	0.2927
4.015	3.836	5.025	2.445	5.173	2.202	0.8327	5.504	0.2087
3.974	3.999	5.005	2.403	5.223	2.204	0.7913	5.419	0.1144
3.933	4.186	4.990				0.7500	5.349	0.3251

4. Discussion

Our data represent correctly represent the optical properties to be expected from air-exposed uranium oxide. There is clearly a substantial difference between our and Schoenes' data. One possible reason (mentioned by Schoenes in reference [1]) is the fact that the reflectance is strongly affected by the perfection of the surface. Ellipsometry is on the other hand is not strongly affected. Another possible reason could be the formation of a hyperstoichiometric layer on the surface of our sample – even though our Raman spectrum indicates that our sample is stochiometric UO_2. Manara [5] determined Raman spectra of stoichiometric and hyperstoichiometric UO_2 using 514 nm light and observed – albeit at much lower resolution than shown in figure 2 - a detectable up-shift in the peak at 445 cm^{-1} only for hyperstochiometry above $UO_{2.05}$. No such shift is detectable in figure 3; hence it is important to determine whether Raman spectroscopy at 632nm and ellipsometry analyze the same region of the sample, and to calculate the depth of the layer that may have become hyperstoichiometric due to exposure to air.

Exposing UO_2 to air at low temperature results in a two-step reaction: $UO_2 \rightarrow U_4O_9 / U_3O_7 \rightarrow U_3O_8$ with U_3O_7 being preferentially formed on un-irradiated UO_2. The oxidation is controlled by the diffusion of oxygen through the U_3O_7 layer, and the parabolic kinetic data are thus typically fitted to an equation of the form

$$\tau = \sqrt{kt}, \text{ with } \tau = U_3O_7 \text{ layer thickness, cm; k, } m^2/s; \text{ t = time, s} \quad (4)$$

Kinetic data have been acquired since 1957 [6], and critically evaluated in recent reviews [7] [8] [9] resulting in $k=2.014*10^{-7}*\exp[-12534/T$ [8]. That equation predicts an U_3O_7 ($=UO_{2.33}$) layer thickness of 6.5 nm after 25.5 years of air exposure at 20°C. Using our optical constants in figure 4 one can determine the average depth <x> below the surface from which a Raman or ellipsometric

signal originates, and the fraction of the signal that originates from the predicted U_3O_7 layer of ~ 7 nm. Assuming that the angle of incidence from normal to the surface is β (=~0 for Raman, ~ 70° for ellipsometry) , then <x> and the fraction of the signal originating from depth less than 7nm are given by equation 5

$$< x >= \int_0^\infty x \frac{2\alpha(\lambda)e^{-2\alpha(\lambda)x/\cos\beta}}{\cos\beta},\ \lambda = \text{wavelength},\ \alpha(\lambda) = \frac{4\pi k}{\lambda}$$

$$\text{At } \lambda = 632 \text{ nm},\ \beta = 0 \text{ (Raman)}, \text{ k} = .3,\ < x > \ = 83.82nm$$

$$\text{Fraction of the Raman signal from the first 7 nm} = 8\% \text{ for } \lambda = 632 \text{ nm} \qquad (5)$$

$$\text{At } \lambda = 632 \text{ nm},\ \beta = 70(\text{ellipsometry}), \text{ k} = .3, < x > \ = 28.1nm$$

$$\text{Fraction of the ellipsometry signal originating from the first 7 nm} = 22\% \text{ for } \lambda = 632 \text{ nm}$$

Allen et al. [10] showed that while U_4O_9 results in up-shift of the peak at 445cm^{-1}, U_3O_7 produces only a small and very broad feature at 445cm^{-1}. Since (see equation 5) only 8% of our Raman signal in figure 2 originates from the 7 nm thick U_3O_7 layer it is likely that the broadening would not be apparent in figure 2. The ellipsometric data, however, may be influenced by the optical properties of the hyperstoichiometric layer, since 22 % of the ellipsometric signal originates from that layer. However, for energies less than 1.35 eV, we determine k to be less than .15, and only 8.2% of the ellipsometric signal originates from the first 7 nm; hence our n and k values below 1.35 eV represent the properties of $UO_{2.0}$. Schoenes data, in contrast, show ε2 to be zero below 2 eV, implying that $UO_{2.0}$ is transparent to red (and longer wavelength) light. At energies above 3 eV, our data are clearly be substantially influenced by a 7nm thick U_3O_7 layer. The sample will be re-analyzed after either vacuum annealing at 1700 K, or after grazing-angle ion-ablating 10 nm from the surface.

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